Microwave detection of protonated SO_2 in two isomeric forms

Valerio Lattanzi
Michael C. McCarthy
Patrick Thaddeus
Sven Torwirth[a,b]

Harvard-Smithsonian Center for Astrophysics
School of Engineering & Applied Sciences, Harvard University
[a]Max-Planck-Institut für Radioastronomie
[b]I. Physikalisches Institut Universität zu Köln

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What is known about SO_2 ?

- *Astronomical : widely distributed*
  - First astronomical detection in OMC and Sgr B2

    (Snyder et al. 1975)
  - Observed in a variety of environments : planetary atmospheres interstellar and extragalactic regions

    (Martin et al. 2003)
  - Very conspicuous in hot-cores high mass star forming regions. high fractional abundance : 10^{-5}-10^{-6}

    (White & Phillips 1983)
  - Isovalent with S_2O and S_3, other species of astronomical interest
- *Laboratory : extensively studied molecule*
  - Recently rotational spectrum studied through 2 THz

    (Müller & Brünken 2005)
  - Calibration reference in the millimeter and submillimeter wave regions

    (Medvedev et al. 2004)

Why $HOSO^+$?

...in space...

- 15 cations observed in ISM (10% of total)
  - important test of chemical reactions
- 15 sulfur bearing molecules detected in ISM (10% of total)
  - sulfur chemistry poorly understood

...in the lab...

- High Proton Affinity - 676 kJ/mol
- Several new protonated species recently detected in this laboratory
  - carbonyl sulfide ($HSCO^+$)

McCarthy & Thaddeus, JCP, 2007

  - carbon disulfide ($HSCS^+$)

McCarthy et al. JCP, in press

What is known about $HOSO^+$?

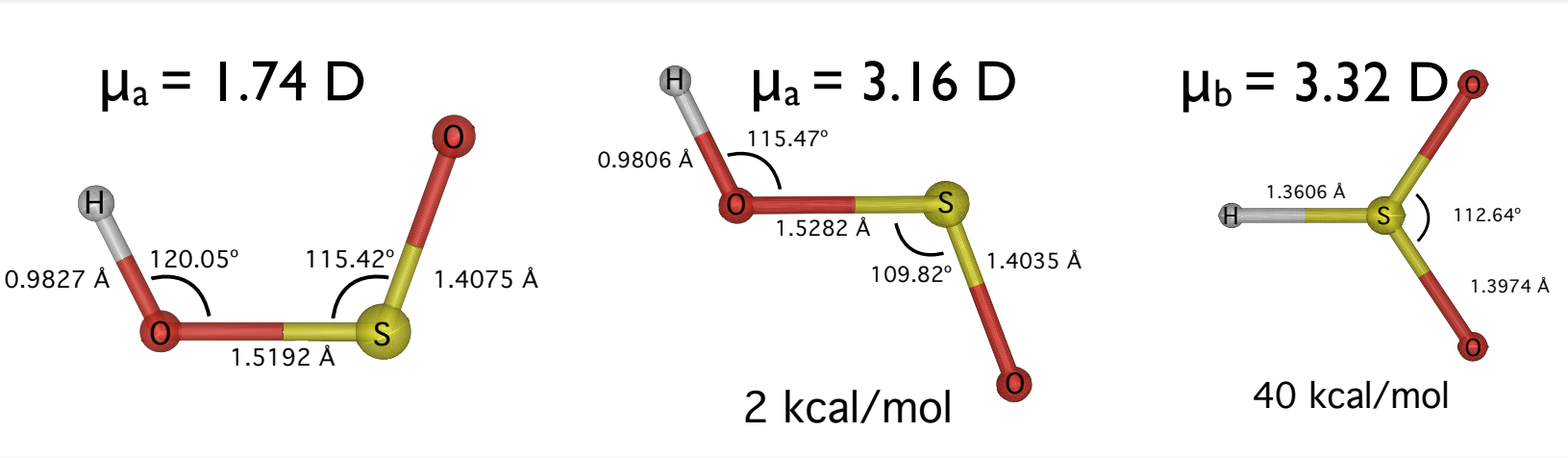
- Astronomically :
  - ...

- Chemically :
  - *Ab initio* calculation at MP2(Full)/6-31+G(d,p) level of theory, but...

(Frank et al. JACS, 1997)

Theoretical calculations

- Three protonated SO_2 isomers



- Both *cis* and *trans* isomers are planar, asymmetric top with C_s symmetry

Theoretical calculations

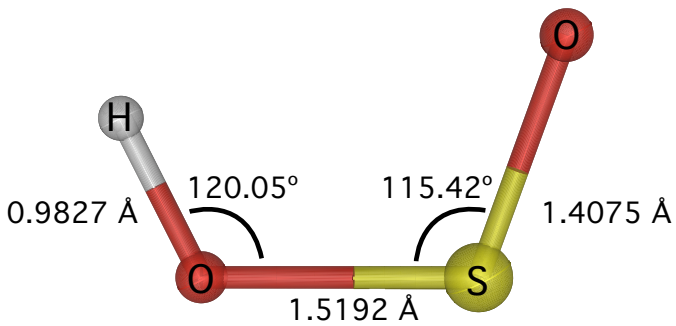
- *Ab initio* calculation performed at the CCSD(T)/cc-pwCQVZ level of theory
- Equilibrium rotational constants corrected for zero point vibrational effects at the CCSD(T)/cc-pV(T+d)Z
- Old and new calculations differ $> 10^{-2}$ Å for bond lengths

Experimental setup

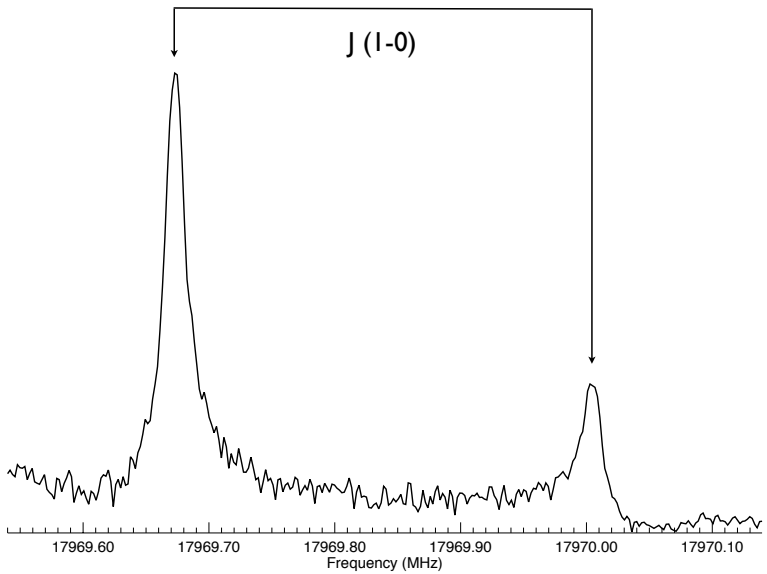
- Detection of the rotational spectra by FTM spectroscopy
  - 5 - 43 GHz
  - 6 Hz pulsed nozzle to inject the supersonic molecular beam ($\sim$ Mach 2)
  - $T_{rot} \sim$ 1-3 K
  - DC discharge of a mixture of sulfur dioxide heavily diluted in H_2 ($\sim$ 1%)

cis-$HOSO^+$

- Fundamental rotational transition $1_{0,1} \rightarrow 0_{0,0}$ @ 18 GHz
- A total of 4 lines assigned, including the two K_a=1

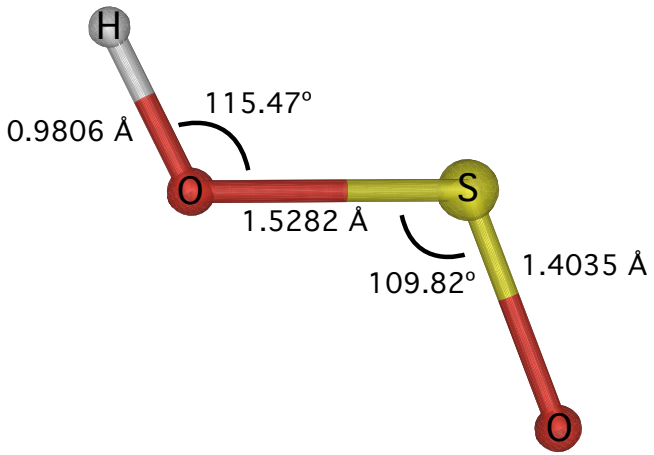


less than 3 minutes integration



trans-$HOSO^+$

- Fundamental rotational transition $1_{0,1} \rightarrow 0_{0,0}$ @ 18 GHz
- A total of 4 lines assigned, including the two K_a=1



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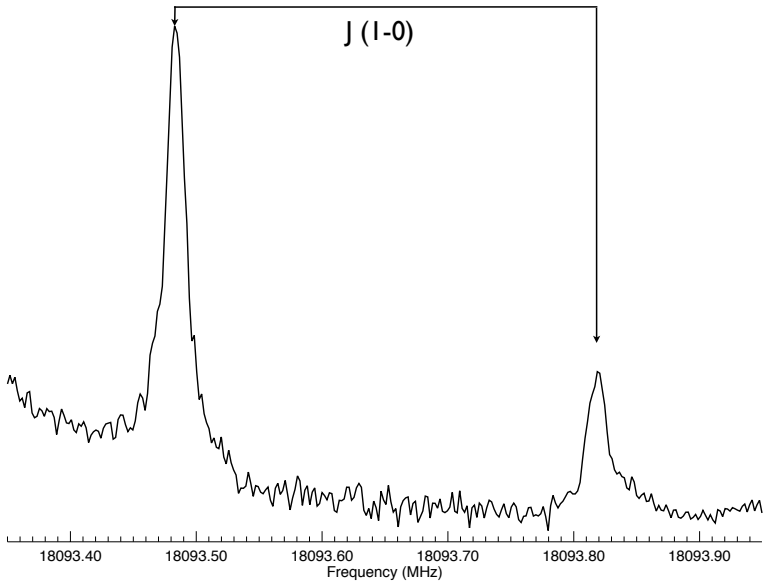

Analysis

- *All the K_a=0 lines found $<$ 0.01% from the ab initio predictions*

cis-HOSO$^+$ rotational constants

Constant	This work	Theoretical
A_0	44187.6(30)	44360.387
B_0	9899.7335(20)	9896.423
C_0	8070.1350(20)	8074.093

Isotopic confirmation

- Isotopic species detection provides crucial confirmation of the main molecule discovery !
- Theoretical rotational constants derived through structure calculation
- Scaling predicts frequencies better than 0.01 %
- 4 lines detected for *cis*-$DOSO^+$; $1_{0,1} \rightarrow 0_{0,0}$ HF resolved
- Detection of $1_{0,1} \rightarrow 0_{0,0}$ of *cis*-$HO^{34}SO^+$ in natural abundance

Conclusion

- Astronomical detection of both isomers could give a good insight into the formation mechanism
- Higher frequency laboratory measurements are planning for the near future
- Deep search for the cm rotational spectrum of *trans*-$DOSO^+$ is in progress
- Protonated SO to follow

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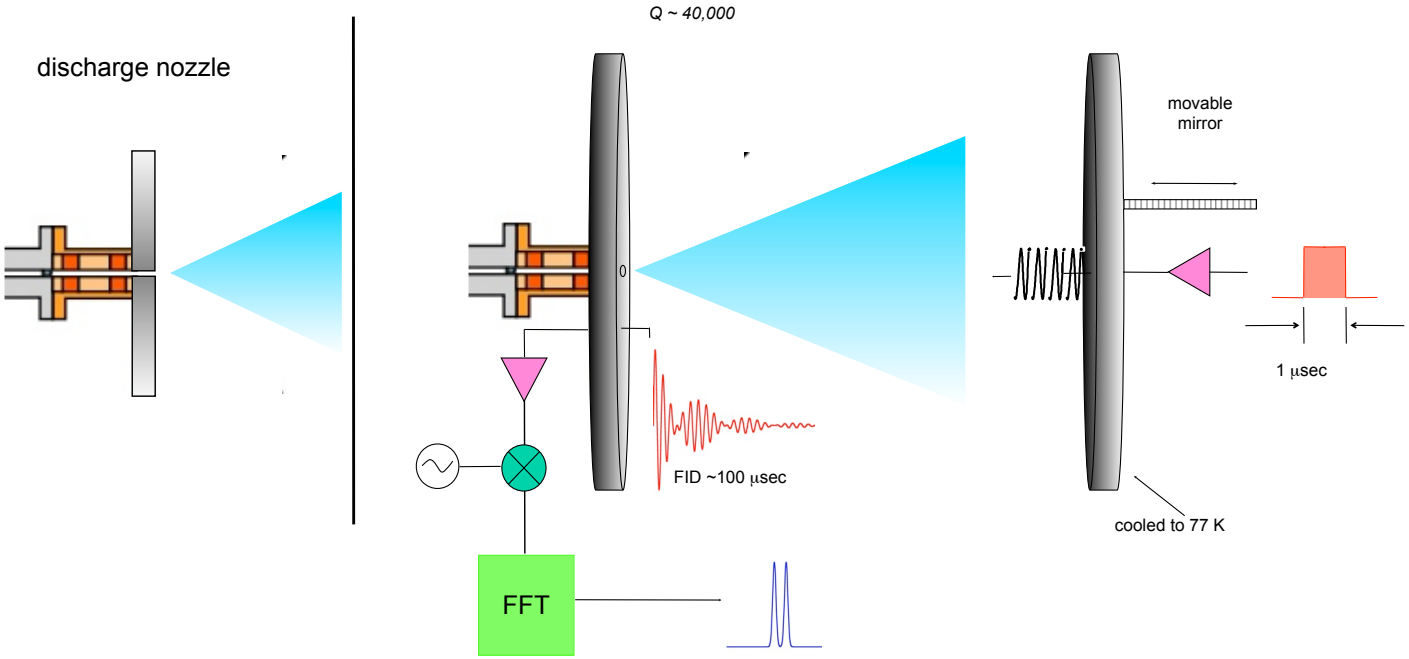
FTM spectrometer



FTM lines

	HOSO$^+$		*cis*-DOSO$^+$	*cis*-HO^{34}SO$^+$
$J'_{K'_a,K'_c} \rightarrow J_{K_a,K_c}{}^a$	*cis*	*trans*		
$1_{0,1} \rightarrow 0_{0,0}$	17969.837	18093.653	17222.366	17925.153
$2_{0,2} \rightarrow 1_{0,1}$	35868.210	36116.879	34355.243	
$2_{1,2} \rightarrow 1_{1,1}$	34110.247	34357.705	32543.881	
$2_{1,1} \rightarrow 1_{1,0}$	37769.444	38013.861	36345.799	